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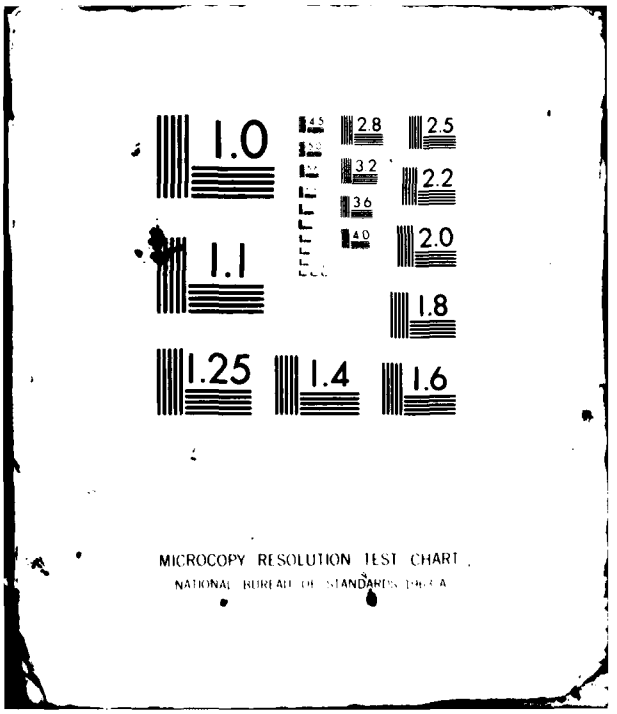
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A STUDY OF STRUCTURAL PHASE TRANSITIONS USING LIGHT SCATTERING TECHNIQUES

Final Technical Report

by

W. Taylor

December 1981

EUROPEAN RESEARCH OFFICE

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Light scattering, phase transitions, soft modes, central peaks, perovskites, lead germanate, potassium selenate, barium manganese fluoride, proustite, silver iodide, lithium diborate.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
This report describes light scattering measurements from a variety of materials which undergo structural phase transitions. The materials studied include $Pb_5Ge_3O_{11}$, $SrTiO_3$, $BaTiO_3$, $RbCaF_3$, $KMnF_3$, KH_2PO_4, KD_2PO_4, K_2SeO_4, $BaMnF_4$, Ag_3AsS_3, AgI and $Li_2B_4O_7$. Effects studied include: the influence of defects; the spectral response of 'soft modes'; the existence of dynamic precursor clusters; central peaks; incommensurate excitations; disorder effects in superionic and other crystals.

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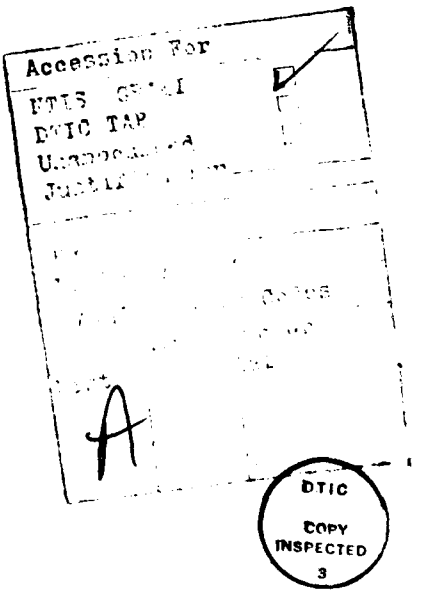

1) Results

(a) Effect of defects on Structural Phase Transitions (SPT's)

i) Lead germanate ($Pb_5Ge_3O_{11}$)

In order to assist the further interpretation of our work on the effects of doping on the Raman spectra of lead germanate we carried out measurements of the temperature dependence of the dielectric constant (ε_c) of barium-doped lead germanate using a novel computer-assisted technique to obtain precise data over a wide temperature and capacitance range. We found that the doping has a very pronounced effect on the dielectric anomaly; the peak in ε_c is shifted to lower temperatures, considerably broadened and reduced in magnitude but passes through a small maximum at around 4% barium. Similar effects have been observed in other mixed ferroelectrics. In contrast, the presence of oxygen impurities in otherwise pure samples, is found to affect only the peak value and not the temperature of the maximum in ε_c.

Results on the pure material show that the quality of the crystals (prepared by RSRE Malvern) is much higher than that from other sources. (Ref. 1).

ii) Perovskites

Earlier studies of a sample of $SrTiO_3$ containing a small concentration of defects showed that modes which are strictly forbidden by symmetry actually contribute to the Raman spectrum by virtue of the symmetry-breaking effects of impurities. New measurements of the low-frequency, low temperature Raman spectrum revealed a strongly temperature dependent low frequency lineshape

for temperatures below 10 K. We believe this to be attributable to a mode which, if it were to condense, would be associated with a ferroelectric phase transition. Since this transition does not occur in pure samples, we were optimistic that further experiments would clarify the connection between the impurity content of the sample and a possible transition below 10 K, but late delivery of a new cryostat and leak problems encountered subsequently delayed work on this project beyond the grant expiry date.

(b) Spectral lineshapes near structural phase transitions

Extensive measurements were made of the soft mode spectrum of $SrTiO_3$ at temperatures below its transition temperature of around 100 K, in order to compare with neutron measurements of the same modes at the same temperatures and to test the theoretical prediction that owing to the effect of 2-phonon scattering on the lineshape, a Raman scattering experiment does not provide a good representation of the one-phonon spectral function close to T_c. The experiments were complicated by the unpredictability of the pattern of tetragonal domains below the phase transition; different domain patterns yield different mode strengths in the Raman spectrum. We tried to circumvent the domain problem by either (i) subtracting spectra taken from different domain patterns to remove unwanted background, or (ii) adding spectra from a single domain pattern to yield and effectively 'single-domain' cross-section. Method (i) proved impossible in practice as the signal/noise ratio was unacceptably degraded. We collected a set of spectra from a single domain pattern in a single polarisation, thereby achieving self-consistency, but not allowing for the

application of method (ii) above. In practice, the effects of resolution corrections to the neutron spectrum and intense quasielastic scattering in the Raman spectrum made the comparison with neutron scattering difficult at all temperatures and impossible in the most interesting region - close to the transition. Attempts to use fixed frequencies, taken from neutron data, to least-squares fit the Raman spectra proved fruitless. The most that can be said is that the difference in frequency over the temperature range 82 - 94 K between the neutron and Raman soft mode measurements is genuine insofar as the simple soft mode model is reasonable.

Work began recently to study spectral lineshapes in potassium dihydrogen phosphate in both its undeuterated (KDP) and deuterated (DKDP) forms. Comparison of the diagonal x(zz)y Raman spectrum, where the first order modes are absent, with the x(yx)y spectrum should reveal the effects of second order scattering on the soft mode lineshape close to T_c. KDP and its isomorphs differ from other much-studied ferroelectrics (e.g. $SrTiO_3$ and $Pb_5Ge_3O_{11}$) in that the critical fluctuations are active in the one-phonon Raman spectrum both above and below the transition.

(c) Temperature dependence of hard modes close to a STP - perovskites

In work on the perovskites $SrTiO_3$, $KMnF_3$ and $RbCaF_3$ we found that the Raman spectra of the latter two (fluoride)-perovskites showed evidence of hard-mode persistence into the cubic phase. These observations were interpreted in terms of precursor-order induced scattering originating from dynamic clusters close to the phase transition. The theoretical treatment makes a connection between this and the central-peak observed in neutron scattering

experiments. (Ref. 2).

In another perovskite, barium titanate, we re-examined the spectra to try to relate the anomalous temperature behaviour and persistence above T_c of the first order modes in the cubic phase to analogous behaviour in other perovskites.

We obtained very high quality spectra of pure barium titanate which however only confirm most of the published data. The conflicting interpretations of the strong A_1 modes (which persist into the cubic phase) have been studied carefully. We conclude that these modes are indeed 1st order modes which are induced by the disorder of the Ti atoms as evidenced by the X-ray studies of Comes and Lambert. These conclusions are supported by Sanjurjo, Katiyar and Porto in an infrared study published in Phys. Rev. B22, 2396, (1980).

(d) Direct measurement of central peak linewidths

Preliminary experiments using the iodine-filter technique and single-pass Fabry-Perot interferometer confirmed the existence of a dynamic central peak in lead germanate and the new triple-pass super-invar interferometer produced good test spectra of the acoustic modes in lead germanate but we were not able to improve on published data.

Attempts to record the off-diagonal dynamic central peak in $SrTiO_3$ were frustrated by the presence of a strong elastic Rayleigh/ parasitic component. Accurate alignment of the triple-pass super-invar interferometer, essential to any central peak experiment, is not easy, and it took some time to obtain high quality test spectra of $SrTiO_3$. These spectra are encouraging, but it may prove necessary to use the iodine absorption cell

technique to complete this work. A preliminary study of the Brillouin spectrum of K_2SeO_4 near its commensurate-incommensurate phase transition did not reveal any strong dynamic central component.

(e) Phase modes in incommensurate systems

i) Potassium selenate (K_2SeO_4)

After the expenditure of some time and effort we succeeded in growing high-quality crystals of potassium selenate. Measurements of the Brillouin spectrum of incommensurate K_2SeO_4 revealed a strong temperature dependence in the strengths of the Brillouin modes and in the frequency of one of the modes. These experiments were time consuming due to the hygroscopic nature of the material which necessitates frequent re-polishing of the surfaces, and therefore dictates that a steady supply of new samples be available.

A crystal of K_2SeO_4 was cut with <101> faces in order to measure the behaviour of the Brillouin spectrum of modes propagating along the incommensurate (100) axis. In this geometry neutron scattering experiments suggest that the phason excitation should have a frequency of .2 cm^{-1} but attempts to find a mode in this range proved negative; the scattering between the acoustic modes is very weak, and theory suggests that phason scattering will be weak. We were, however, able to measure significant frequency and intensity changes in the acoustic mode spectrum at the lock-in (II → III) transition contrary to the results of other workers. No extra excitations were seen at the I → II transition, and the experiments did not, therefore, reveal the hoped-for 'phason' excitation.

ii) Barium manganese fluoride ($BaMnF_4$)

Extensive measurements were made of the room temperature Raman spectrum of $BaMnF_4$, with better polarisation and signal/noise characteristics than any published work. This data facilitated a classifiation of the transverse and longitudinal modes of A_1, B_1 and B_2 symmetry and we now believe our assignment of the first order modes at 295 K to be as good as can be achieved. (Refs. 4 and 5) We attempted to extract an archetypal soft mode from the low frequency spectrum by further fitting of model lineshapes. In particular we used a model allowing for coupling of the soft mode to other modes on the soft mode branch. This model has produced soft modes in lead germanate where divergence of the damping parameter took over from lowering frequency close to T_c, within a simple model but attempts to 'force' a soft mode and thus avoid divergent damping parameters in $BaMnF_4$ proved signally unsuccessful forcing us to the conclusion that the prediction of the Landau theory, that the fluctuations of the amplitude of the incommensurate modulation should yield a $\vec{q} = 0$ soft mode below T_c, is incorrect. (Refs. 3 and 5)

(f) Other work

i) Proustite (Ag_3AsS_3)

In collaboration with Dr. G.L. Paul of the University of New South Wales, W. Taylor completed a study of the low-temperature Raman spectra of proustite (Ag_3AsS_3) which includes very clear spectra of an unusually low frequency soft mode associated with the 58 K phase transition. (Ref. 6). Work on this material is continuing.

ii) Superionic structural transitions - Silveriodide (AgI)

After some time devoted to crystal preparation, redesign of the Fabry-Perot system and commissioning a new computer control program (at University of California, Irvine), preliminary experiments were started on the crystal AgI. Initial technical difficulties and problems with the light sensitivity and fragility of the samples delayed progress but eventually we obtained satisfactory spectra of the acoustic modes. No low frequency mode related to hopping motion of the silver ions was found but a discontinuity in one of the acoustic mode frequencies was observed. (Ref. 7)

iii) Lithium diborate ($Li_2B_4O_7$)

Reports of an elastic anomaly in this useful material near room temperature prompted us to carry out a series of measurements of its Raman spectrum at various temperatures. No evidence of a phase transition was found but the spectra and mode assignments will be published as the first ever report on the Raman spectra of this compound. (Ref. 8)

iv) Interfacing to the HP85 microcomputer

This system now successfully controls both the Raman spectrometer and the Fabry-Perot interferometer simultaneously, while allowing other procedures such as spectrum display and plotting to be carried out at the same time.

By constructing a system based on 'bus interrupts' we have achieved a high level of flexibility; the controller spends relatively little time actually controlling the experiment, and

is largely free to perform calculations or graph plotting. This is achieved through the high level of intelligence resident in the HP6942A multiprogrammer, which can perform a specified function or functions initiated by the controller, freeing the controller immediately after initiation. Correct sequencing of events is ensured by the multiprogrammer's ability to signal that a function is complete and that a new function should be initiated.

The communication link between the microcomputer and the ICL 2970 mainframe computer is also now fully operational; this allows direct on-line transfer of data files from the HP85 disc drive. Our new system thus entirely replaces the previous PDP11 system which was time-shared with other users.

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